DOI: 10.1002/ejic.200900321

Semi In Situ Synthesis of NHTS: A New Hollow Titanium Silicalite Modified by a Noble Metal

Chunfeng Shi,[a] Bin Zhu,[a] Min Lin,*[a] and Jun Long*[a]

Keywords: Zeolites / Hydrothermal synthesis / Titanium silicalite / Noble metals / Palladium / Mesoporous materials

A new hollow titanium silicalite with a noble metal incorporated into it (denoted as NHTS) was synthesized by a semi in situ method. This NHTS has intraparticle voids and exhibits bifunctional catalytic performance. It was characterized by various techniques, and its catalytic performance for the direct epoxidation of propylene was investigated. The results show that NHTS, with a highly ordered MFI topological and hollow structure, together with a noble metal, can be employed in catalytic oxidations.

Introduction

Onsite hydrogen peroxide (H_2O_2, HP) production followed by HP conversion to organic oxides without refining (namely direct oxidation technology, one-pot process) is regarded as an attractive route for the production of organic oxides, and has the potential to reduce the initial capital needed and to reduce production costs.[1,2] The key point of direct oxidation technology is the design and preparation of the catalysts used therein, which are bifunctional and mostly consist of noble metals and titanium silicalite. At present, the main difficulty of the process is to increase the efficiency of HP synthesized in situ,[3] which makes the process economically unviable for the moment. Therefore the aim is to improve the efficiency of HP production, by preparing new catalysts or renewing customary catalysts, and to simultaneously maintain the oxidation activity of titanium silicalite.[4,5]

In most heterogeneous catalytic oxidations, diffusion is the main factor that influences the catalytic reactions. The use of porous catalysts, for example zeolites, allows rapid diffusion of the products out of the particles, but the presence of micropores in the particles might limit the diffusion of the reactant molecules to internal catalytic sites. As far as we know, with the same particle size and pore radii for porous catalysts, molecular diffusion in catalysts with hollow structures occurs at a faster rate than that in catalysts with a solid structure, as molecular diffusion to internal active sites is limited to a lesser extent.[6,7] One object of our research is to design and prepare such porous catalytic materials with hollow structures. Here, we provide another new hollow-structure titanosilicate that acts as a bifunctional catalyst, which is synthesized by the addition of noble metals to the mixture, with the formation of an intermediate, under basic conditions. This method is called the "semi in situ" method and is one in which the new hollow titanium silicalite has a noble metal incorporated into it (denoted as NHTS, a new titanium silicalite modified by a noble metal). The sample was characterized by various techniques and its catalytic performance for the epoxidation of propylene with H_2 and O_2 as oxidants was also investigated.

Results and Discussion

The results of the XRF analysis of NHTS is as follows: PdO 0.48%, SiO_2 97.80%, and TiO_2 1.72%. These results indicate that the incorporation of Pd within the framework of titanium silicalite does not break its chemical composition represented in the oxide form.

The X-ray diffraction pattern of NHTS is shown in Figure 1(a). The main diffraction peaks are those for the typical TS-1 molecular sieves with an MFI topological structure.[8,9] This result indicates that the combination of Pd into the framework of TS-1 has no influence on its crystal structure. The relative crystallinity of NHTS is calculated according to the method described in the literature[10] with TS-1 as a standard sample. There are only slight intensity differences between them, which indicates that the incorporation of Pd does not severely affect its ordering. Furthermore, it can be seen that the XRD pattern does not show any obvious characteristic signals for noble metal Pd, which indicates the very high dispersion of Pd into NHTS.[11,12]

---

[a] State Key Laboratory of Catalytic Material and Reaction Engineering,
Research Institute of Petroleum Processing (RIPP), SINOPEC, Beijing 100083, P. R. China
Fax: +86-10-82368801
E-mail: chfshi@yahoo.com.cn

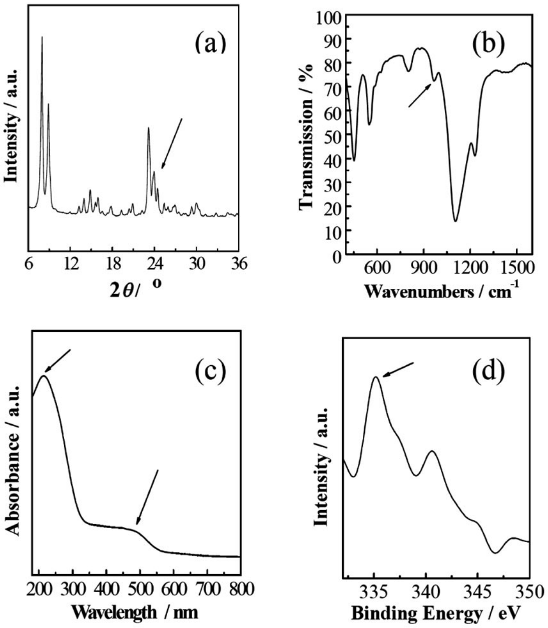


Figure 1. (a) XRD pattern, (b) FTIR spectra, (c) UV/Vis spectra, and (d) XPS Pd 3d spectra of NHTS.

Figure 1(b) shows the FTIR spectra of NHTS, the main absorption bands are observed at 550, 800, 1100, and 1230 cm^{-1}, which is in agreement with those in the FTIR spectra of TS-1 with a MFI structure reported in the literature.[13] It is well known that an absorption band near 960 cm^{-1} is assigned to the stretching mode of the $[SiO_4]$ tetrahedral bond with Ti atoms and may be considered as the fingerprint of framework titanium.[14] For our NHTS, the characteristic “fingerprint” band at about 960 cm^{-1} is clearly detected; however, the peak shifts to 969 cm^{-1}. This is likely caused by the change of the coordination structure or by the vibration of Ti^{IV} atoms, which may be induced by the incorporation of a noble metal into the framework of NHTS.

The intraframework, isolated, tetrahedral Ti^{4+} ions in NHTS are further verified by UV/Vis spectroscopy [Figure 1(c)]. It can be seen that the main UV absorption band is at 210 nm, which clearly shows the existence of intraframework, isolated, tetrahedral Ti^{4+} ions.[15] One broad absorption band centered at about 480 nm, assigned to the absorption of a noble metal species,[16] also appears. This is consistent with the observations of Shetti et al.[16] and also proves that the noble metal species are included in NHTS.

Pd in the zero oxidation state exhibits XPS Pd 3d peaks at a binding energy of 335.0 eV, while PdO (+2 oxidation state) at 336.8 eV.[17] XPS Pd 3d peaks of NHTS are at a binding energy of 335.2 eV [Figure 1(d)], which indicates that the oxidation state of Pd in NHTS is more likely to be zero, Pd^0. As the values of the binding energy differ slightly, there may be some interactions between Pd and the titanosilicate matrix, which leads to a slight change in the electronic structure of Pd.

The TEM micrograph of NHTS is shown in Figure 2(a). The particles of NHTS have an average particle size of 0.3 μm. The majority of particles exhibit a hollow structure (with intraparticle voids), while TS-1 has a solid structure (not shown here). The above phenomena also show that the semi in situ process leads not only to the introduction of Pd into NHTS, but also to the formation of intraparticle voids, which is proved further by N_2 adsorption/desorption isotherms measurements. Furthermore, the TEM image does not show any obvious characteristic particles of pure Pd species, which indicates the very high dispersion of Pd in NHTS. This result is in agreement with the XRD analysis.[18,19]

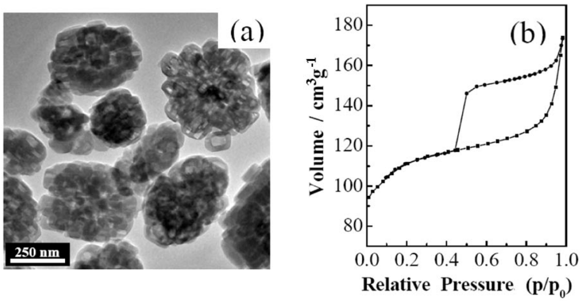
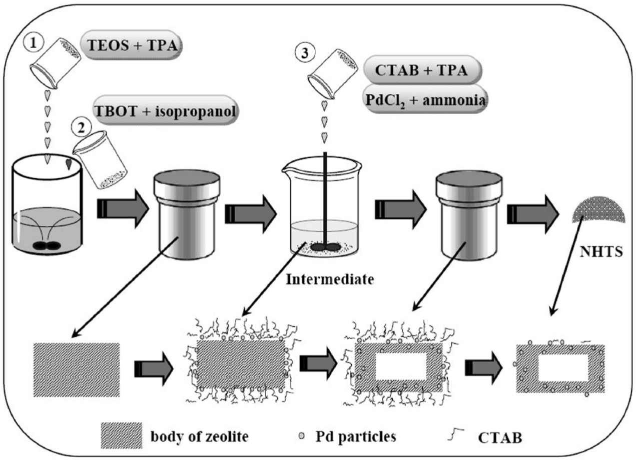


Figure 2. (a) TEM image and (b) N_2 adsorption/desorption isotherm of NHTS.

It can be seen from Figure 2(b) that NHTS shows typical adsorption/desorption curves of type IV (according to IUPAC classification) with an obvious hysteresis loop, which suggests that NHTS has a hollow structure.[7] The porous parameters such as total BET surface area and pore volume of NHTS are given as 416 m^2/g and 0.31 cm^3/g, respectively; the values for the corresponding microporous parts are 380 m^2/g and 0.17 cm^3/g, respectively.

The “semi in situ” synthesis procedure, the role of surfactant, and the formation of voids in the NHTS crystals are illustrated by a simplified scheme (see Scheme 1). The Si source, Ti source, Pd source, etc. have not been added in the same step, therefore the whole synthesis process is named “semi in situ”. The intraparticle voids in the NHTS crystals are formed during the dissolution–recrystallization reprocess,[7] and the role of surfactant is as a protective agent, so as to avoid the aggregation of noble metal particles deoxidized by the reducing agent.

TS-1 and Pd particles are not catalytically active in the epoxidation of propylene under the conditions used, while NHTS exhibits a high activity. For example, after 1 h, the catalytic activity (propylene oxide concentration, C_{PO}) is 2.6%, and the selectivity is 92.5% (the selectivity for propylene oxide, S_{PO}; the other two products are propylene glycol monomethyl alcohol ethers and 1,2-propanediol). Moreover, higher epoxide yields are obtained with longer reaction times, for instance, after 6 h, the value of C_{PO} for NHTS is 3.6%, and the S_{PO} selectivity decreases slightly to 90.1%. At the same time, the formation of HP from H_2 and O_2 under the reaction conditions was proven directly in a separate experiment without the addition of propylene, it



Scheme 1. Simplified scheme of the "semi in situ" synthesis of NHTS and the role of surfactant.

can therefore be deduced that the formation of HP could occur over the Pd particles, while propylene epoxidation occurs over the Ti species in the framework of NHTS. This may indicate that TS-1 has no catalytic activity since it only contains Ti and therefore could not form HP from H_2 and O_2 in situ and that Pd particles also have no catalytic activity since it has no Ti species to epoxidize propylene. This also proves that the direct propylene epoxidation process involves onsite HP production followed by the oxidation of propylene to PO by HP. It can be expected that the TS-1[10] would be active if it was impregnated with Pd (denoted as Pd/TS-1), but the catalytic activity of Pd/TS-1 (C_{PO} value of only 0.7% for 1 h and 1.9% for 6 h) is not comparable to that of NHTS. The results show that NHTS exhibits a higher catalytic performance, can catalyze more propylene and yield more PO. This phenomenon can be attributed not only to the stable incorporation of a noble metal into the framework of titanium silicalite during the semi in situ synthesis process, but also to the hollow structure of NHTS formed during the process. The results have also shown that NHTS with a hollow structure is an excellent catalyst for the preparation of PO by means of direct oxidation technology.

Conclusions

NHTS, a new hollow titanium silicalite structure with a noble metal incorporated into it, was synthesized by the addition of a noble metal to a mixture of tetraethyl orthosilicate and tetrabutylorthotitanate, with the formation of an intermediate, under basic conditions. The semi in situ synthesized NHTS exhibits a very ordered MFI topological structure, which is hollow, with a noble metal incorporated into it. This structure type makes NHTS useful, with potential application in industry for use in catalytic oxidations.

Experimental Section

Synthesis: All reagents were of analytical grade and used as received. NHTS was synthesized in a semi in situ manner according to the following steps. (1) Tetraethyl orthosilicate (TEOS, 36 g) was mixed thoroughly with tetrapropylammonium hydroxide (TPAOH, 14.5 g) solution and distilled water (110 g). After hydrolysis at 75 °C for 2 h, a solution of tetrabutylorthotitanate (TBOT, 0.8 g) and 2-propanol (9.1 g) was added whilst stirring. The mixture was stirred at 75 °C for 3 h and then transferred into an autoclave at 170 °C for 2 d. The crystallization mixture was filtered, washed with distilled water, dried at 120 °C for 3 h, and calcined at 550 °C in air for 4 h. An intermediate was obtained. (2) The intermediate was mixed with hexadecyltrimethyl ammonium bromide (CTAB) and a TPAOH solution containing $PdCl_2$ and $NH_3·H_2O$ in a weight ratio (in g) of 100:10.0:0.1:1.0:4.5:250 for intermediate product/TPAOH/CTAB/$PdCl_2$/$NH_3·H_2O$/water. After stirring the mixture for 2 h, $N_2H_4·H_2O$ was added. The mixture was then transferred to an autoclave and the reaction was carried out at 180 °C for 36 h. After cooling and depressurizing, routine filtration, washing, drying and calcination at 550 °C in air for 5 h, NHTS was obtained.

Characterization: X-ray fluorescence analysis (XRF) was performed on a Rigaku 3271E X-ray fluorescence spectrometer. Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer. Fourier Transform Infrared (FTIR) spectra were recorded on a Nicolet 8210 infrared spectrometer. Diffuse reflectance UV/Vis (UV/Vis) spectra were obtained with a spectrometer Perkin–Elmer Lambda 20 UV/Vis spectrometer. Transmission electron microscopy (TEM) experiments were performed with a Tecnai G^2F20S-TWIN electron microscope. The nitrogen isotherms were measured by using a Micromeritics ASAP 2010M system, specific surface areas were determined from the linear part of the multipoint BET equation and by the t-plot method, and the pore volumes (total, micropore and mesopore) were calculated from the isotherms by BJH and by the t-plot method. X-ray photoelectron spectroscopy (XPS) was performed with a PHI Quantera Scanning X-ray Microprobe.

Catalytic Test: Catalytic tests were performed in a stainless steel autoclave lined with a Teflon beaker. The catalyst (1.0 g), methanol (40 g), and deionized water (2 g) were charged to the reactor. When the pressure reached 0.8 MPa after propylene was fed into the reactor, the vessel was pressurized with hydrogen and oxygen (mol ratio 1:1) successively until the pressure in the reactor reached 2.0 MPa. The slurry was heated from room temperature to 40 °C under pressure and with vigorous stirring. The reactor was kept at 40 °C for 1 h and 6 h, and then was cooled down to a temperature below 10 °C. At the end of the reaction, the catalyst was filtered off. The liquid phase analysis was performed on an Agilent 6890N gas chromatograph (GC).

Acknowledgments

We are grateful for the financial support from the State Basic Research Project "973" from the Ministry of Science and Technology of People's Republic of China (Grant number of 2006CB202508). The authors would also like to thank Prof. X. T. Shu, Prof. X. Q. Wang, Prof. J. Fu, Prof. X. H. Mu, and Prof. Y. B. Luo in RIPP for their very kind suggestions.

---

[1] N. Yap, R. P. Andres, W. N. Delgass, *J. Catal.* **2004**, *226*, 156–170.
[2] T. A. Nijhuis, T. Visser, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2005**, *44*, 1115–1118.
[3] Q. Chen, E. J. Beckman, *Green Chem.* **2007**, *9*, 802–808.
[4] G. Mul, A. Zwijnenburg, B. van der Linden, M. Makee, J. A. Moulijn, *J. Catal.* **2001**, *201*, 128–137.

[5] L. Cumaranatunge, W. N. Delgass, *J. Catal.* **2005**, *232*, 38–42.

[6] Y. Wang, A. Tuel, *Microporous Mesoporous Mater.* **2008**, *113*, 286–295.

[7] Y. Wang, M. Lin, A. Tuel, *Microporous Mesoporous Mater.* **2007**, *102*, 80–85.

[8] M. Taramasso, G. Perego, B. Notari, *US Patent*, Enichem, **1983**, 4410501.

[9] E. Duprey, P. Beaunier, M.-A. Springuel-Huet, *J. Catal.* **1997**, *165*, 22–32.

[10] M. Lin, X. T. Shu, X. Q. Wang, B. Zhu, *CN Patent*, SINOPEC, **2002**, 1089279C.

[11] C. Shi, R. Wang, G. Zhu, S. Qiu, J. Long, *Eur. J. Inorg. Chem.* **2005**, 4801–4807.

[12] C. Shi, R. Wang, G. Zhu, S. Qiu, J. Long, *Eur. J. Inorg. Chem.* **2006**, 3054–3060.

[13] P. Fejes, J. B. Nagy, J. Halasz, A. Oszko, *Appl. Catal. A: Gen.* **1998**, *175*, 89–104.

[14] G. Ricchiardi, A. Damin, S. Bordiga, C. Lamberti, G. Spano, F. Rivetti, A. Zecchina, *J. Am. Chem. Soc.* **2001**, *123*, 11409–11419.

[15] M. R. Boccuti, K. M. Rao, A. Zecchina, G. Leofanti, G. Petrini, *Stud. Surf. Sci. Catal.* **1989**, *48*, 133–135.

[16] V. N. Shetti, P. Manikandan, D. Srinivas, P. Ratnasamy, *J. Catal.* **2003**, *216*, 461–467.

[17] W. Shen, Y. Ichihashi, M. Okumura, Y. Matsumura, *Catal. Lett.* **2000**, *64*, 23–25.

[18] C. Shi, M. Xin, R. Wang, Y. Xie, L. Hu, L. Xu, R. Zhang, G. Zhu, S. Qiu, *Chem. J. Chin. Univ.* **2005**, *26*, 1198–1201.

[19] C. Shi, L. Wan, R. Wang, J. Long, G. Zhu, S. Qiu, *Chem. J. Chin. Univ.* **2006**, *27*, 1194–1197.

Received: April 8, 2009